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(54) Plasticised PVC compositions

(57) Esters of fatty acids having the formula RCOOR^1 wherein the groups R and R^1 which may be the same or different represent alkyl or alkenyl groups comprising from 6 to 24 carbon atoms have been discovered to be used as lubricants in PVC compositions which comprise a phosphate ester as a plasticiser or flame retardant because their use reduces the evolution of unpleasant odours during manufacture of the compositions and in applications such as extrusion. The novel PVC compositions find particular value in coating of wire and cable where they reduce odour and may enable the use of a composition which does not contain any heavy metals. The preferred ester is stearyl stearate.

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PLASTICISED PVC COMPOSITIONS

This invention relates to novel polyvinyl chloride resin compositions which comprise a phosphate ester plasticiser and to wire and cables which are surrounded by an insulating coating based upon such a resin.

Polyvinyl chloride and copolymers thereof such as polyvinyl chloride/acetate are rigid and brittle in their unplasticised state. They can be formed into durable flexible resins by compounding them with a plasticiser and these plasticised resins find use in a large number of applications and are manufactured on a large scale. A variety of additives are used as plasticisers for polyvinyl chloride (hereinafter PVC) among the most common being phthalate esters; adipate esters; sebacate esters; trimellitate esters; citrate esters; sulphonates; polyesters; chloroparaffins and phosphate esters. The plasticised resins are mostly flammable and it is common practice to formulate resins which exhibit a degree of flame resistance. The most common methods of producing a flame resistant plasticised composition are to incorporate a synergist such as antimony oxide or sodium antimonate into the resin or to employ a phosphate ester plasticiser or a combination of these two approaches.

The use of phosphate esters in PVC formulations is well established and has been used inter alia in formulations used to coat electrical wire and cables. One disadvantage which is associated with the use of such formulations particularly where the phosphate ester is an aromatic ester based on an alkylated phenol, is a tendency for an objectionable odour to be noted whilst the polymer is being processed and also to a lesser degree in the wire or cable which is produced.

There is thereby a need in the art for a plasticised PVC resin which exhibits flame retardant properties and which does not evolve an objectionable odour either during processing or in the finished product.

We have now discovered that plasticised PVC compositions having improved odiferous properties can be produced by careful choice of the lubricant which is conventionally incorporated into such compositions. We have discovered that the use of certain esters of fatty acids which are substantially neutral reduces or eliminates the problem of odour formation. Accordingly from one aspect this invention provides a plasticised polyvinylchloride resin which comprises a phosphate ester plasticiser and an effective quantity of a lubricating ester having the formula RCOOR^1 wherein the groups R and R^1 which may be the same or different represent an alkyl or alkenyl group comprising from 6 to 24 carbon atoms.

Preferably the groups R and R^1 comprise at least 8 carbon atoms and more preferably each will contain at least 12 carbon atoms. The groups R and R^1 will preferably comprise a total of from 24 to 40 carbon atoms.

The groups R and R^1 may represent a hexyl group, a heptyl group, an octyl group, a decyl group, a dodecyl group, a tetradecyl group, a hexadecyl group or an octadecyl group.

Esters having the formula RCOOR^1 are widely available as articles of commerce and may readily be produced by the reaction of an acid of formula RCOOH with an alcohol of formula

R^1OH . Suitable acids from which useful esters may be derived include caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. Examples of alcohols from which useful esters may be derived include hexanol, heptanol, octanol, decanol, dodecanol, lauryl alcohol, myristyl alcohol, cetyl alcohol and octadecyl alcohol. These acids and alcohols may be synthetic products or they may be derived from natural sources. The use of esters of formula $RCOOR^1$ wherein either or both of the groups R and R^1 represent a mixture of alkyl and/or alkenyl groups is within the scope of the present invention. The use of acids of formula $RCOOH$ and alcohols of formula R^1OH wherein the groups R and R^1 comprise an average of from 6 to 24 and preferably an average of at least 12 carbon atoms is also within the scope of this invention. The effectiveness of a particular ester in conjunction with a particular resin formulation and in a particular processing operation may be determined by routine experiment.

The esters which are used in this invention are preferably substantially neutral i.e in general they will have an acid number of less than 1.0 mg KOH /g. The use of esters having an acid number of less than 0.5mg KOH/ g is preferred .

The polyvinyl chloride resins into which these ester lubricants are incorporated are preferably homo polymers of polyvinyl chloride or copolymers of polyvinyl chloride incorporating other monomers such as vinyl acetate , acrylic acid and esters of acrylic acid. However the invention also finds use in resins derived from other vinyl chlorides such as in polyvinylidene dichloride ,chlorinated polyvinyl chloride and chlorinated polyethylene. Blends of these resins may also find use in the compositions of this invention.

The phosphate ester plasticisers used to impart flame resistance to polyvinylchloride resins are well known in the art. Useful esters include alkyl phosphates; aryl phosphates; alkaryl phosphates and mixed alkyl / aryl phosphates. The preferred phosphates are neutral esters derived from aliphatic alcohols, phenols or alkyl substituted phenols or any mixture of these compounds. The aliphatic alcohols from which the phosphates may be derived include saturated alcohols comprising from 4 to 18 carbon atoms. The alkyl substituted phenols may be obtained from synthetic or from natural sources. Examples of phosphates derived from natural sources of phenol include mesityl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, trixylyl phosphate and xylyl diphenyl phosphate. Examples of phosphates obtained from synthetic sources are those produced by the phosphorylation of a mixture of alkylated phenols which has been produced by the reaction of phenol with an alkylating agent comprising three or four carbon atoms such as propylene or iso butylene. Examples of mixed alkyl / aryl phosphates include octyl diphenyl phosphate; isodecyl diphenyl phosphate and dodecyl diphenyl phosphate. The invention finds particular application in those compositions where the phosphate is a triaryl phosphate obtained by the phosphorylation of a mixture of alkylated phenols which has been obtained by the alkylation of phenol with propylene.

The polyvinyl chloride composition typically comprises from 10 to 100 parts by weight of the plasticiser for each 100 parts by weight of the resin.. Preferably the plasticiser is a phosphate ester but mixtures of the phosphate ester with other plasticisers may be employed.

The resin compositions of this invention may contain from 0.1 to 5.0 parts by weight of a lubricant. The lubricant in the compositions of this invention preferably comprise at least 50% by weight and more preferably at least 80% by weight and most preferably at least 95% by weight of an ester having the formula RCOOR^1 . However these esters may be used in combination with other known lubricants. A wide variety of compounds are known to be useful e.g paraffin wax, stearic acid, calcium stearate, stearyl alcohol, stearamide and glycerylmonostearate. The compositions of this invention are preferably free from metal salts and in particular from metal stearates such as calcium stearate and lead stearate. In a preferred embodiment the compositions of this invention are substantially free from any heavy metal. Where other lubricants are present they are preferably present as only a minor proportion of the lubricant component as their presence may tend to cause the evolution of unwanted odours.

The compositions of the present invention may also comprise other conventional ingredients well known to the art. For example they may comprise fillers such as calcium carbonate, magnesium carbonate, mica, aluminium trihydrate and clay; they may comprise a heat stabiliser such as a salt of lead, tin, calcium, zinc, barium, aluminium and magnesium (or mixtures of these salts); an impact modifier such as a methacrylate butadiene styrene terpolymer; a hydrogen chloride adsorber such as an aminocrotonate; an antioxidant such as bisphenol A; or a smoke suppressant such as zinc borate or molybdenum trioxide or a pigment such as titanium dioxide, carbon or a dyestuff. The compositions may also comprise other flame retardant additives such as antimony oxide, sodium antimonate or a chloroparaffin.

The compositions of this invention may also be blended with other polymeric materials in order to vary the properties of the final composition in a manner which is known in the art. For example they may conveniently be blended with polyvinyl acetate, with ethylene/vinyl acetate copolymers and with acrylic butadiene rubbers.

The compositions of this invention may conveniently be prepared by any method which permits uniform mixing of the ingredients. Typically the ingredients will be dry blended to homogeneity and the dry blend fluxed at elevated temperature and then extruded, cooled and dried.

The compositions of this invention may be used in any of the conventional applications of PVC. They find particular value in applications which involve extrusion of the PVC composition or other processing which involves exposure to elevated temperature. The compositions find particular application in the formation of insulating coatings around wire and cables. They can be used in the conventional processing operations wherein the coating is extruded through a cross head die which can be either a pressure die or a tubing die the wire or cable being strung through the centre of the die. Wire and cable which is coated with a composition of the invention exhibits improved odiferous properties and constitutes another aspect of this invention.

The invention is illustrated by the following examples:-

Example One

A series of resin compositions were made up using 100 parts by weight of a polyvinyl chloride resin (Evipol SH7020) and 30 parts by weight of an isopropylated phenol phosphate (Reofos 95). The remaining ingredients of each composition is summarised in Table 1. The ingredients were mixed in a Turbomixer with an end temperature of 105° C followed by kneading in a Buss 100mm diameter extruder at 135° C and finally re-extruded at 200° C. The extrudates were allowed to cool to room temperature. The cool resins were presented to a panel of assessors who compiled a ranking of which resins were strongly odorous and which were virtually odourless. The results of this assessment is included in Table 1. (Evipol is a Trade Mark of EVC. Reofos is a Trade Mark of FMC Corporation.).

Table 1

	1	2	3	4	5	6	7	8
Evipol SH7020	100	100	100	100	100	100	100	100
Reofos 95	30	30	30	30	30	30	30	30
Diisodecyl phthalate	20	20	20	20	20	22.5	22.5	22.5
Calcium carbonate	20	20	20	40	-	20	20	20
Magnesium hydroxide	20	20	20	-	40	20	20	20
Electrical Grade Clay	10	10	10	10	10	-	-	-
Zinc Oxide	3	3	3	3	3	3	3	3
Dibasic lead phthalate	9	9	9	9	9	5	5	5
Bisphenol A	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Lead stearate	1.0	-	-	-	-	1.0	-	-
Calcium stearate	0.5	0.4	0.4	0.4	0.4	0.5	0.5	0.5
Stearyl stearate	-	1	1.0	1.0	1.0	-	1.0	1.0
Oxidised polyethylene wax	-	-	1.0	-	-	-	-	-
Aluminium trihydrate	-	-	-	-	-	45	50	-
Oxygen Index	-	31.5%	-	31.0%	32.0%	-	35.0%	31.0%
Odour	Yes	No	Yes	No	No	Yes	No	No

CLAIMS

- (1) A plasticised polyvinyl chloride resin comprising a phosphate ester plasticiser and an effective quantity of a lubricating ester having the general formula RCOOR^1 wherein R and R^1 which may be the same or different represent alkyl or alkenyl groups having from 6 to 24 carbon atoms.
- (2) A composition according to claim 1 characterised in that the groups R and R^1 each comprise an average of at least 12 carbon atoms.
- (3) A composition according to either of claims 1 or 2 characterised in that the groups R and R^1 comprise a total of from 24 to 40 carbon atoms.
- (4) A composition according to any of the preceding claims characterised in that the lubricating ester has an acid value of less than 1.0mg/KOH/ g.
- (5) A composition according to any of the preceding claims characterised in that it comprises from 0.1 to 5.0 parts by weight of a lubricant.
- (6) A composition according to claim 5 characterised in that the lubricant comprises at least 95% by weight of an ester or esters having the formula RCOOR^1 .

- (7) A composition according to any of the preceding claims characterised in that it is substantially free from lubricating metal salts.
- (8) A composition according to claim 7 characterised in that it is substantially free from any heavy metal.
- (9) A composition according to any of the preceding claims characterised in that the phosphate ester plastiser is one which has been obtained by the phosphorylation of a mixture of alkylated phenols which mixture has been produced by the reaction of phenol with an alkylating agent comprising 3 or 4 carbon atoms.
- (10) A composition according to claim 9 characterised in that the phosphate ester is one which mixture has been obtained by the phosphorylation of a mixture of alkylated phenols which has been produced by the alkylation of phenol with propylene.
- (11) An insulated wire or cable having an insulating coating which is characterised in that said coating is formed from a composition according to any of claims 1 to 10.
- (12) A composition according to any of claims 1 to 10 substantially as hereinbefore described with reference to the foregoing examples.



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Claims searched: 1 to 11

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): C3K KEC KEZ KFA KLA; C3V VDF VDM VDQ VDT VDX
Int Cl (Ed.6): C08K 5/00, 5/10, 5/101; C08L 23/00, 23/26, 23/28, 27/00, 27/02,
27/04, 27/06, 27/08, 27/22, 27/24
Other: ONLINE: CLAIMS, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0587104 A2 The Geon Company see the claims and page 10, lines 18 to 23	
A	WPI Abstract Accession No: 78-77387A/43 & JP530108147 A (MITSUBISHI MONSANTO KK) 20 September 1978 see abstract	
A	WPI Abstract Accession No: 84-071647/12 & JP590025827 A (MITSUBISHI MONSANTO KK) 09 February 1984 see abstract	

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